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Article

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A Novel Multi-Charged Draw Solute That Removes Organic Arsenicals from Water in a Hybrid Membrane Process

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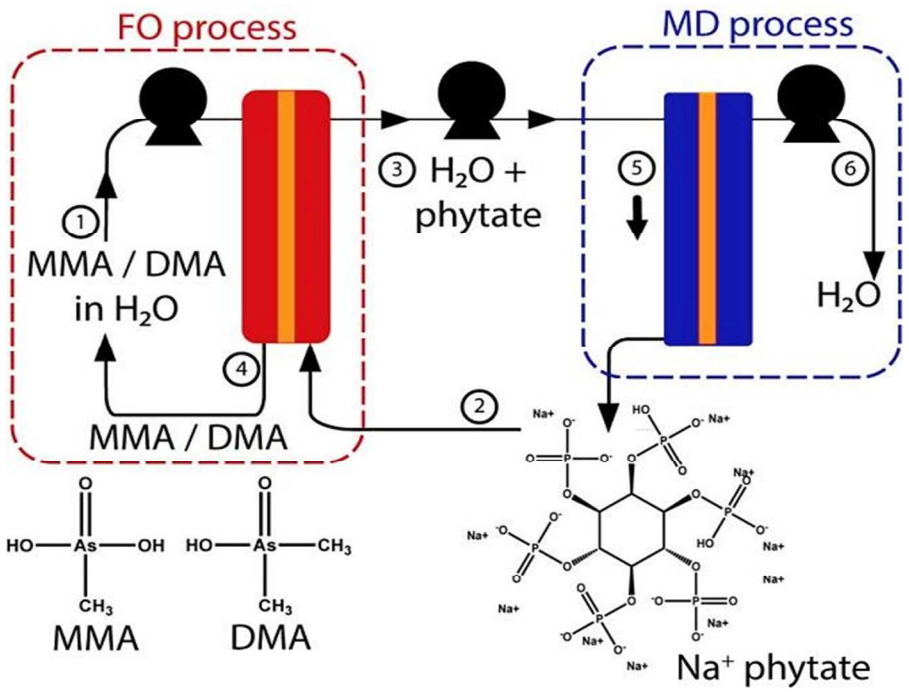
ABSTRACRT: The potential of forward osmosis for water treatment can only be maximized with suitable draw solutes. Here a three-dimensional, multi-charge draw solute of decasodium phytate (Na_{10}-phytate) is designed and synthesized for removing organic arsenicals from water using a hybrid forward osmosis (FO) – membrane distillation (MD) process. Efficient water recovery is achieved using Na_{10}-phytate as a draw solute with a water flux of 20.0 LMH and negligible reverse solute diffusion when 1000 ppm organic arsenicals as the feed and operated under ambient conditions with FO mode. At 50 ˚C, the novel draw solute increases water flux by more than 30 % with water fluxes higher than 26.0 LMH on the FO side, drastically enhancing

water recovery efficiency. By combining the FO and MD processes into a single hybrid process, a 100% recovery of Na_{10}-phytate draw solute was achieved. Crucially, organic arsenicals or Na_{10}-phytate draw solutes are both rejected 100% and not detected in the permeate of the hybrid process. The complete rejection of both organic arsenicals and draw solutes using hybrid membrane processes is unprecedented; creating a new application for membrane separations.

■ TOC Art



■ INTRODUCTION

Arsenic contamination of water resources arise from their natural geological presence in deep underground water sources or from anthropogenic activities such as mining, farming, and wood preservation.[1-3] Arsenic can exist as toxic (inorganic or organic) and nontoxic (organic content in seafood) forms.[1,3] The toxicity of arsenic depends on valence state, solubility, physical state and

purity, rates of absorption and elimination. In general, the toxicity of arsenicals is as follows: Inorganic trivalent > organic trivalent > inorganic pentavalent > organic pentavalent > elemental arsenic.[4-6] The toxicity of various arsenic forms guides the design of current arsenic removal technologies. Traditionally, inorganic arsenic compounds were perceived to be more toxic and potent than organic arsenicals.[4,7] Hence, conventional technologies such as adsorption, ion exchange, coagulation, and membrane separations (nanofiltration, reverse osmosis, and electrodialysis) were investigated for removing inorganic arsenicals.[6-8]

Despite the extensive applications of these technologies for arsenical removal, the following problems are widely present. Large volumes of arsenic-rich sludge and waste can be generated using adsorption and coagulation,[2,9-11] while membrane separation technologies consume large amounts of energy.[6,12-14] The removal of organic arsenic has become increasingly important as methyl derivatives of arsenic that are omnipresent in agriculture (monomethylarsenic – MMA, dimethylarsenic – DMA) present a carcinogenic risk.[4] Moreover, inorganic arsenic compounds can convert into methylated arsenicals under appropriate conditions.[7] Clearly, there is a need to develop a green and cost-effective bespoke technology for removing organic arsenicals.

Here we propose to use a hybrid forward osmosis (FO) – membrane distillation (MD) process to remove organic arsenics (Figure 1). FO-MD is an economical and sustainable technology to treat wastewater,[15] concentrate protein solutions,[16] and desalination.[17] This technology separates water from dissolved solutes (contaminants or proteins) using the operating principle underpinning FO processes while recovering the draw solute using MD. An osmotic pressure difference is first generated by a concentration gradient using a “draw” solution with higher concentration of dissolved solutes in relation to the feed solution. Water from the feed solution permeates across the membrane, while the contaminants are retained in the FO feed. The FO

permeate now contains a dilute mixture of water and draw solute that requires MD to recover the draw solute while producing high purity water. Clearly, the crux of this hybrid process is the draw solutes.[18] Suitable draw solutes can enhance FO performance, i.e. achieving high water recovery whilst avoiding secondary contamination at lower costs, and recovered. Conventional draw solutes such as NaCl,[19] $MgCl_2$[20] and glucose saccharide[20] have been deployed for removing inorganic arsenics, but to minimal effect. This is attributed to either low water permeation flux, or/and severe reverse solute diffusion.

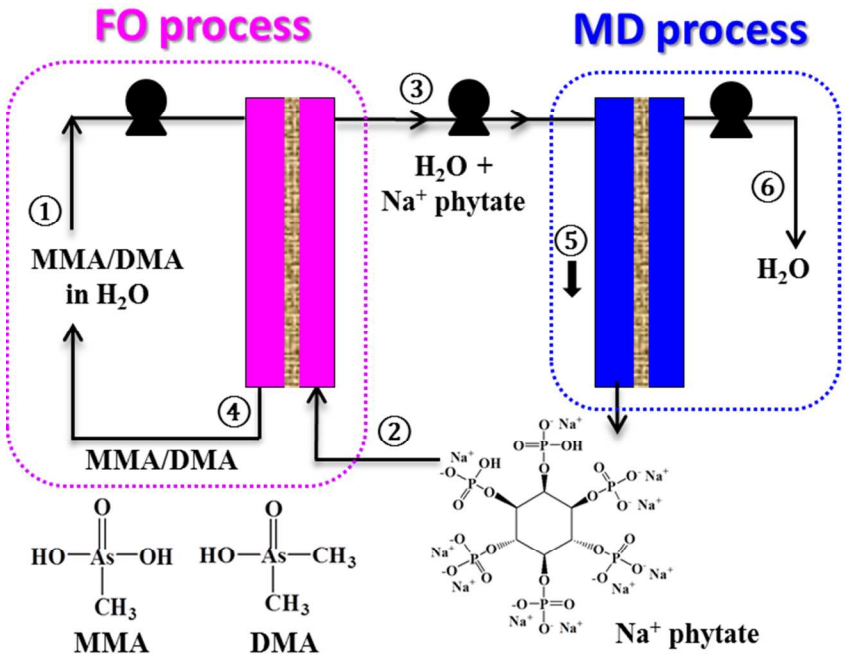


Figure 1. Using Na_{10}-phytate draw solute to treat water that contains MMA and DMA via a FO process. Subsequently, the draw solute is dehydrated and regenerated using an in-line MD process.

Excellent draw solutes that optimize FO processes are typically pH-neutral, easily ionized compounds that generate large osmotic pressures.[21,22] These compounds produce a neutral solution that does not degrade the membrane during FO, whilst providing a large driving force for water transport. Draw solutes with a suitable spatial configuration and high ionization degree

are critical for producing a high water recovery and minimizing reverse solute diffusion across the membrane in FO.[22] Guided by these requirements, we design and synthesize a novel phytate (Na_{10}-phytate) and demonstrate the advantages of this new compound as a draw solute to remove organic arsenicals from water. First, water fluxes of up to 20 LMH (FO mode) are achieved at room temperature when Na_{10}-phytate is deployed in single FO processes. Second, we observed negligible reverse solute diffusion during MMA or DMA removal even at 50 ˚C. Finally, we show that MMA or DMA can be completely removed from water while the Na_{10}-phytate draw solutes are fully recovered and regenerated.

■ MATERIALS AND METHODS

Syntheses of Na_{10}-Phytate. Na_{10}-phytate was synthesized through the neutralization reaction between phytic acid and NaOH. The experimental details were given in the supporting information (SI).

Determination of the Sodium ion Numbers in Na_{10}-Phytate. The number of sodium ions in the synthesized sodium phytate was determined via acid-base titration. The detailed information was provided in the SI.

Characterization of Na_{10}-Phytate. Elemental analyses, the size distribution of Na_{10}-phytate in its aqueous solution, and thermogravimetric analysis (TGA) measurement were used to determine the chemical composition of Na_{10}-phytate and its state in solution prior to the FO applications. The experimental details were included in the SI.

Determination of the Physicochemical Properties of the Na_{10}-Phytate Solution. The physicochemical properties of the Na_{10}-phytate solution were determined by analyzing their relative viscosity and osmotic pressures. Details were provided in the SI.

FO Processes. The FO experiments were carried out through a bench-scale FO set-up as established elsewhere.[23] Commercial HTI flat sheet membranes and home-made thin-film composite (TFC) FO membranes fabricated on polyethersulfone (PES) hollow fibers (TFC-PES)[24] were both used in the FO experiments. The detailed experimental conditions were provided in the SI.

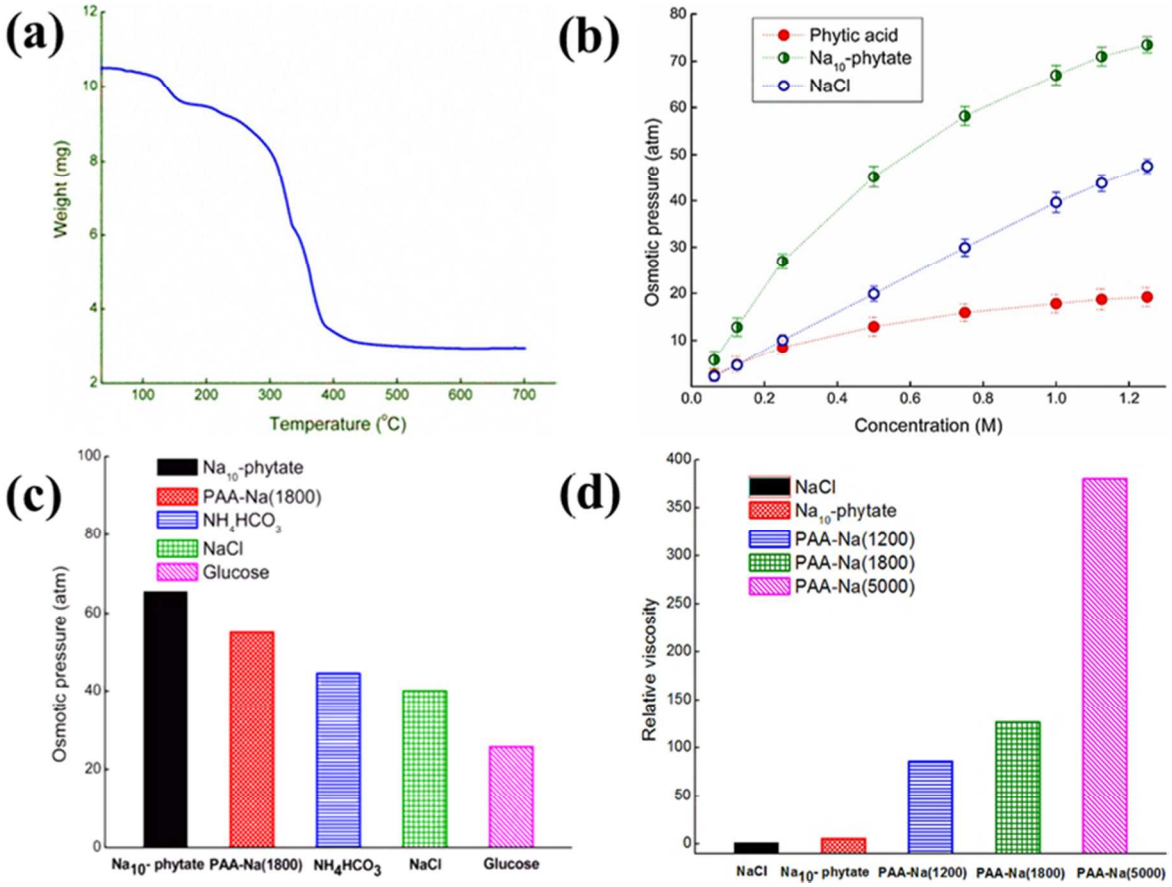
Preparation and Analyses of MMAs and DMAs Solutions. The MMAs and DMAs solutions were prepared from CH_4AsNaO_3 and $(CH_3)_2AsNaO_2$, respectively. The pH values of these solutions were maintained using HCl and NaOH. The experimental details of the MMAs/DMAs solution preparation and analyses were included in the SI.

Regeneration of Na_{10}-Phytate Solute. An MD set-up with home-made PVDF hollow fiber membranes[25] was employed to concentrate the diluted Na_{10}-phytate solution after FO. The experimental details were disclosed in the SI.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Na_{10}-Phytate. Phytic acid, a hexaphosphate polyacid, was neutralized with a known volume and molar concentration of sodium hydroxide (NaOH) to produce a three-dimensional, multi-charge decasodium phytate (Na_{10}-phytate) neutral draw solute. The leftover NaOH solution was titrated with hydrochloric acid (HCl); revealing a 1:10 ratio of phytic acid to sodium hydroxide i.e. there are 10 Na^+ ions in the phytate. Thermogravimetric analysis (TGA) was used to confirm the elemental composition of the phytate developed here in this work. Thermal decomposition of Na_{10}-phytate occurred in two stages. The first stage corresponds to a release of water molecules between 122 – 155 ˚C; accounting for a weight loss of 9.5 wt. % (Table S1). The second stage at 205 – 398 ˚C correlates to the decomposition of 63.8 wt. % of dehydrated organic phosphate salt (Figure 2a). The residue

114 (26.7 wt. %) comprises mainly sodium oxides. Weight losses associated with these two stages
115 are in excellent comparison with theoretical calculations carrying crystal water molecules.



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117 **Figure 2.** (a) TGA analysis of Na_{10}-phytate demonstrating its thermal stability up to 205 ˚C. (b)
118 The osmotic pressures of the precursor compound – phytic acid, conventional draw solute –
119 NaCl, and the novel draw solute developed in this work – Na_{10}-phytate. (c) An osmotic pressure
120 comparison of Na_{10}-phytate with traditional draw solutes. (d) A relative viscosity comparison of
121 Na_{10}-phytate with other draw solutes.

122 Important material characteristics that govern applications as FO draw solutes include osmotic
123 pressure and relative viscosity. We observe that both osmotic pressure and relative viscosity of
124 Na_{10}-phytate increase non-linearly with higher concentrations (Fig. 2b, Fig. S1). This can be
125 ascribed to the relatively large configuration and chemical composition of Na_{10}-phytate. The

hydrophilic functional groups of Na_{10}-phytate can ionize into multi-charge anions and multiple cations in aqueous solutions. Predicted by the Van't Hoff equation,[26] the dissociation of Na_{10}-phytate into multiple ionic species increases the number of solute particles in the aqueous solution; generating an osmotic pressure (66 atm) which is 65 % larger than that of NaCl at 1.0 M, the conventional draw solute in FO (Figure 2b). At low concentrations, salts dissociate completely into multiple ionic species; generating large increments in osmotic pressures.[27] This is impeded at higher concentrations. However, the osmotic pressure generated by 1.0 M of Na_{10}-phytate is significantly higher than those of synthetic draw solutes such as magnetic nanoparticles,[28] polyelectrolytes,[29] hydrogels[30] and many others[22,31] (Figure 2c). Meanwhile the relative viscosity (η_r) of Na_{10}-phytate is at least 60 % lower than polyelectrolytes[29] (Figure 2d), and is comparable to NaCl. Compounds with a reduced relative viscosity are preferred as draw solutes for FO processes as less internal concentration polarization will be caused and water molecules can easily diffuse across the membrane towards the permeate side. The good thermal stability, high osmotic pressure, and low relative viscosity of Na_{10}-phytate are ideal for FO.

Na_{10}-phytate as a FO Draw Solute. Initial screening tests (Figure 3) indicated that FO is optimized with a home-made thin film composite (TFC) – polyethersulfone (PES) hollow fiber membrane.[24] Regardless of membrane orientation (the active layer facing feed solution i.e. FO mode or the active layer facing draw solution containing 0.5 M of Na_{10}-phytate – pressure retarded osmosis (PRO) mode), the water flux of a TFC-PES membrane is 3 times higher than that of a commercial flat sheet membrane from HTI. Coupled with an insignificant salt leakage rate, the TFC-PES membrane in FO mode is ideal for FO water treatment. The drastically higher water flux is ascribed to membrane structural configuration where the thin TFC selective layer supported on a porous PES substrate has lower water transfer resistance relative to the dense and

149 thick HTI membrane.[24] Meanwhile the spatial structure and chemical composition of Na_{10}-
150 phytate contribute to a negligible reverse solute diffusion. In Na_{10}-phytate, the evenly-distributed
151 phosphates around an aromatic carbon ring develop a three-dimensional structure that form
152 hydrogen-bond with water molecules in the aqueous solution (Figure S2a). This supramolecular
153 structure inhibits reverse diffusion; minimizing leakage rates. The size distribution of the
154 supramolecular network falls in a range much larger than that of an FO membrane pore size
155 which accounts for the negligible leakage of Na_{10}-phytate (Figure S2b).
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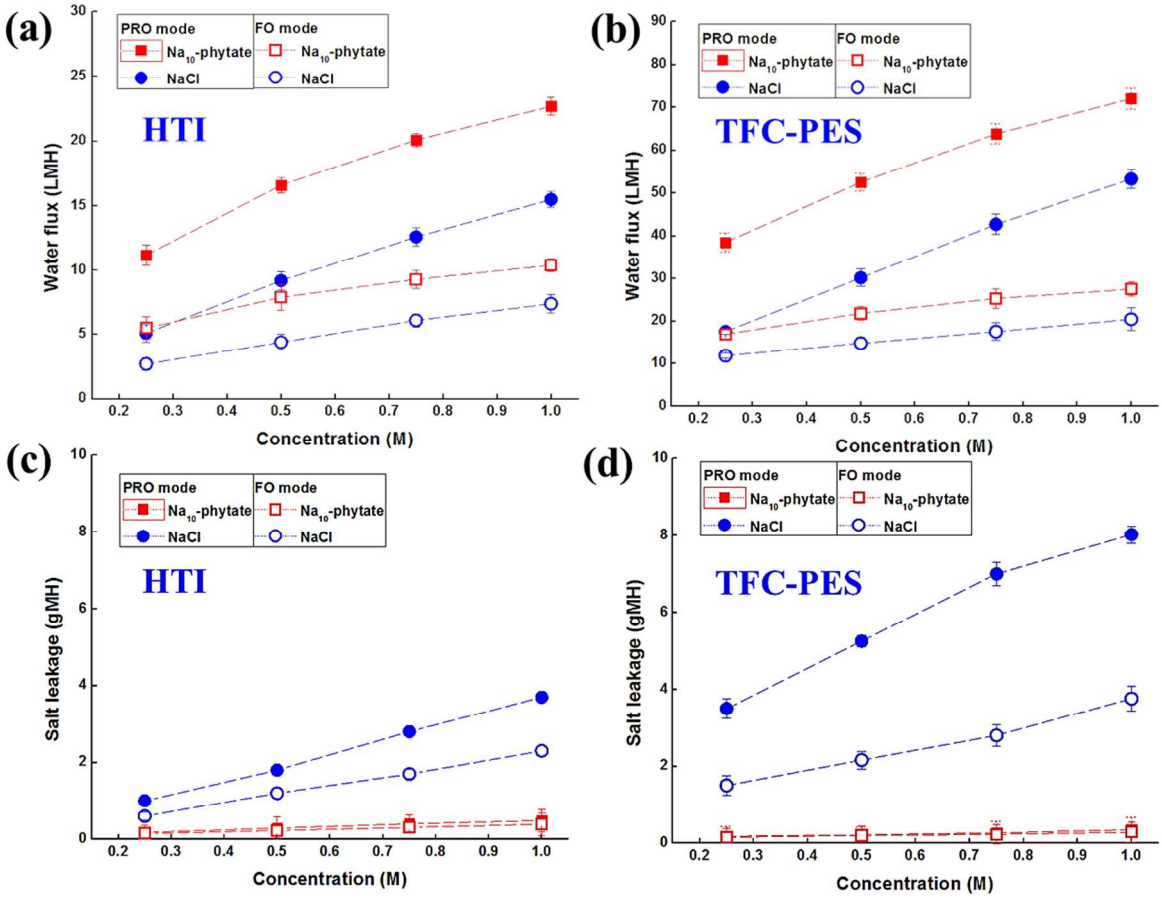

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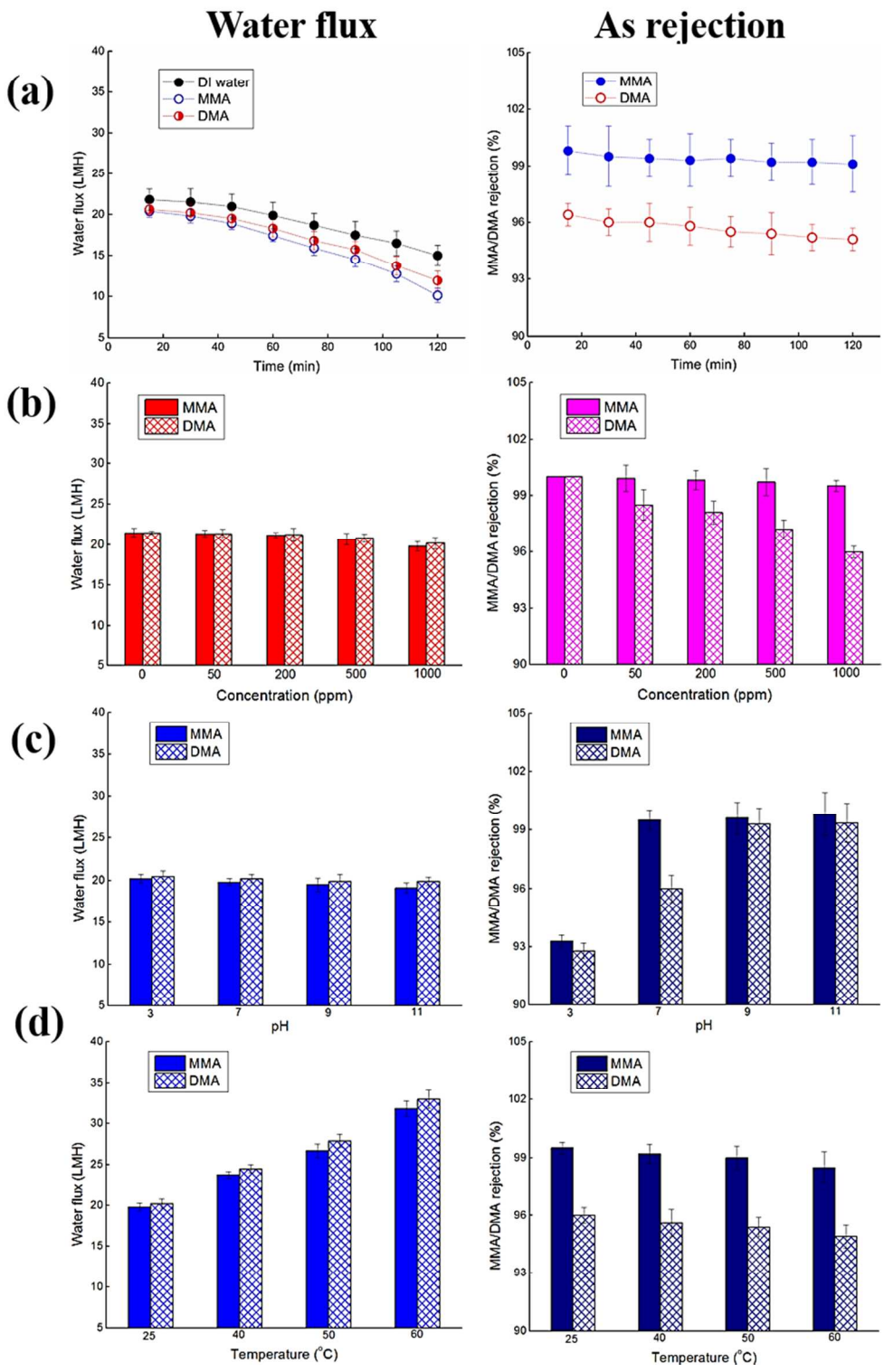
158 **Figure 3.** Effects of draw solute concentration, membrane and membrane orientation on FO performance:
159 (a) water flux of HTI membrane; (b) water flux of TFC-PES membrane; (c) salt leakage of HTI
160 membrane; (d) salt leakage of TFC-PES membrane. DI water as the feed solution.

We investigated the impact of Na_{10}-phytate as a draw solute to remove organic arsenicals in a FO process using TFC-PES hollow fiber membranes at FO operation times between 20 to 120 mins, MMA or DMA concentrations ranging from 0 – 1000 ppm, pH between 3 to 11, and temperatures from 25 to 60 ˚C. These parameters are key for creating an osmotic pressure differential across the membrane to drive FO water treatment. Longer operation times (20 to 120 min) reduced water flux by 20 % with the DI water feed, possibly due to water transfer concentration polarization and/or membrane fouling (Figure 4a). Water flux is reduced by 35 and 45 % with 1000 ppm of DMA or MMA, respectively. Organic arsenicals in the feed solution enhance feed osmotic pressure; reducing the net driving force across the membrane, hence further decreasing water flux. The higher concentration of anions in a MMA solution (relative to DMA solution) can dissociate into more ionic solute particles;[9] generating a slightly higher osmotic pressure. Thus, a lower water flux was observed with MMA present in the feed solution. The high anion concentration in MMA solutions creates a stronger charge repulsion with the surface of the electronegative TFC-PES membrane; rejecting more than 99.5 % of MMA.



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176 **Figure 4.** FO performances (water flux and organic As rejection) for removing MMA or DMA from
177 water using TFC-PES hollow fiber membranes at various operating conditions: (a) 20 – 120 mins of

operation time; (b) 0 – 1000 ppm MMA or DMA in deionized water; (c) pH 3 – 11; and (d) temperature between 25 to 60 ˚C. Experimental conditions for each parameter are shown in the Supporting Information.

Different MMA concentrations did not impact on both water flux and rejection rates (Figure 4b). However, higher DMA content in the feed solution reduced the rejection rate of organic arsenicals to less than 96 %. Neutral DMA solution consists 14 % neutral species, and 86 % monovalent anions.[9] Higher DMA content will increase the number of neutral DMA; hence reducing the rejection rate. The ratio of neutral species to anions in MMA/DMA solutions is also sensitive to pH values (Figure 4c). As pH of a MMA feed solution changes from acidity (3) to alkalinity (11), the neutral species are converted into various anions;[9] hence reducing water flux due to a lower driving force attributed to enhanced osmotic feed pressures but increasing MMA rejection rates. Since DMA solution consists more neutral DMA species than MMA solution, the increase in pH from 3 to 11 will only slightly reduce water flux. Higher temperatures will also enhance the osmotic pressure differentials that consequently increase water flux (Figure 4d). Ideally, to remove 1000 ppm of MMA or DMA more effectively from water, the FO process must be conducted under neutral conditions with a higher temperature. To fully optimize the benefits of FO for removing organic arsenicals, the draw solutes must be recovered/regenerated.

Regeneration of Na_{10}-phytate Draw Solute. Membrane distillation (MD) is a proven technology for regenerating draw solutes such as hydroacid complexes,[32] polyelectrolytes,[15] and thermosensitive polymers[17] from dilute FO permeate solutions. Different from FO processes where draw solution concentration significantly impacts on water flux, temperature dominates water transport in MD.[33] This is also observed here when aqueous solutions containing Na_{10}-phytate at different concentrations were deployed in a single MD process using home-made

polyvinylidene fluoride (PVDF) hollow fiber membranes.[25] The increase in water flux due to increasing temperatures can be attributed to the exponential generation of higher water vapor pressures. The impacts of both Na_{10}-phytate concentration and operation time on water flux were negligible (Figure S3).

By combining the FO and MD processes into a single hybrid process, we report complete recovery of Na_{10}-phytate draw solute whilst producing 100 % water (Figure 5). The water flux of this hybrid process at 50 ˚C is higher than 26.0 LMH on the FO side; sufficient to handle large quantities of wastewater that are typically associated with industrial-scale operations.[34-36] This FO-MD hybrid technology is more efficient that single FO processes for dehydrating dilute MMA/DMA feed solutions. This is because the MD process can immediately concentrate the FO permeate consisting of Na_{10}-phytate draw solute. The combination of our novel Na_{10}-phytate draw solute with a hybrid FO-MD process demonstrates a simple and effective technology for removing organic arsenicals. Additional complex processes such as pre-oxidation[37] and operation in acidic conditions[38] are not required in this FO-MD process, while side reactions of MMA conversion into more toxic inorganic species[39] is inhibited. The combination of our novel Na_{10}-phytate draw solute with FO-MD hybrid process surpasses the water flux and organic arsenical rejection of current technologies.[1,6,8]

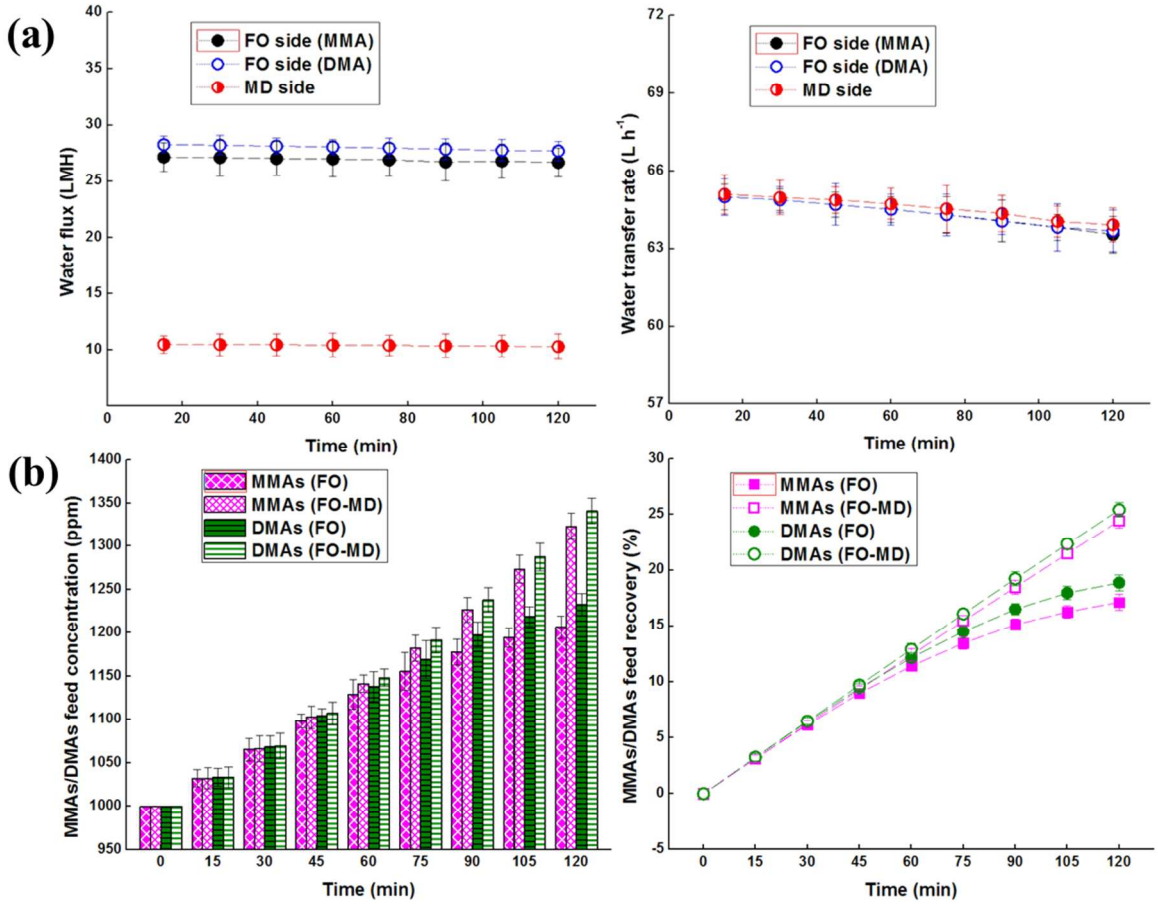

Figure 5. (a) The water flux and water transfer rate, (b) concentrations and rejection rates of organic arsenicals from water of a FO-MD hybrid process using 0.5 M Na_{10}-phytate as draw solute at 50 ˚C. 20 ˚C deionized water was deployed on the MD permeate side.

Using a plant-derived compound, phytic acid, we designed and synthesized a novel draw solute that is suitable for removing organic arsenicals from water in a FO-MD hybrid process. The presence of hydrophilic functional groups arranged in a three-dimensional configuration around an aromatic carbon ring can form supramolecular structures through hydrogen bonds with water molecules that prevent reverse diffusion during FO processes. This draws water across a TFC-PES hollow fiber membrane at rates that can handle industrial-scale quantities of wastewater. The regeneration of the novel Na_{10}-phytate draw solute is optimized using an in-line MD process; streamlining the draw solute recovery process with minimal energy consumption.

Phytate-based draw solutes can be potentially deployed for the removing other types of contaminants during water treatment and are especially suitable for protein enrichment. The negligible reverse diffusion of Na_{10}-phytate in FO can avoid denaturation of impurity-sensitive proteins and produce high-quality products.

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■ ASSOCIATED CONTENT

Supporting Information Available

Materials; syntheses and characterizations of Na_{10}-phytate; the physicochemical properties of Na_{10}-phytate solutions; FO processes; the preparation and analyses of MMAs and DMAs solutions; the regeneration of Na_{10}-phytate; molecular structures of MMAs and DMAs; the TGA spectrum; weight losses of Na_{10}-phytate in TGA measurements; relative viscosity of Na_{10}-phytate and phytic acid; osmotic pressure of Na_{10}-phytate, phytic acid and NaCl; Supermolecular network and size distribution of Na_{10}-phytate in the aqueous solution.

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